Soviet-era science, translated into English

V. V. MOISEEV, E. A. MATEROVA, and A. A. BELYUSTIN

1957

SovietRxiv

View the original and related papers at https://sovietrxiv.org/items/ru-195701.89864

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

Abstract

Full Text

CHEMISTRY

V. V. MOISEEV, E. A. MATEROVA, and A. A. BELYUSTIN

PREPARATION AND INVESTIGATION OF CERTAIN PROPERTIES OF RUBIDIUM AND CESIUM GLASSES

(Presented by Academician A. N. Terenin, 26 XI 1956)

The study of complex silicate glasses in which the only alkali component is rubidium or cesium is of great interest, since it makes it possible to broaden our understanding of the influence of the nature of the alkali ion on the properties of glass and, in particular, to study more fully the processes occurring in the interaction of glass with a solution. As is known, this interaction leads to the appearance of a potential difference at the glass-solution boundary, which is the result of ion exchange between the glass and the solution. Therefore, the investigation of glasses containing rubidium and cesium ions is of great importance for the theory of the glass electrode, expanding the possibilities for obtaining glass electrodes reversible with respect to alkali ions.

However, the preparation of rubidium and cesium glasses entails considerable methodological difficulties, connected above all with the refractory nature of such systems. For this reason, only isolated data on rubidium glasses are available in the literature, and cesium glasses apparently have not been described at all. Thus, Uoterton and Turner (1) obtained a rubidium glass of composition 75% SiO_2, 10% CaO, 15% Rb_2O*, which was melted at a temperature of 1600°; an analogous batch containing cesium oxide instead of rubidium oxide did not even melt at a temperature of 1650°. Perley (2) attempted to melt glasses with a high content of rubidium and cesium especially for studying their electrode properties; however, he was unsuccessful.

It should be noted that in electrode glasses with a hydrogen function, small additions of rubidium and cesium (2-3%) are sometimes used; these hinder the entry of sodium ions into the glass and thereby reduce the alkaline error of the glass electrode (2).

Kracek (3), in studying the liquidus position of cristobalite, also obtained glasses with a small content of rubidium and cesium oxides (3.50-2.59% Rb_2O, 2.34-3.35% Cs_2O).

Since we undertook the preparation of rubidium and cesium glasses in connection with the study of the properties of the glass electrode, an attempt was first made to synthesize a glass of composition: 71% SiO_2, 11% B_2O_3, 3% Al_2O_3,

SovietRxiv

15% Rb_2O, analogous to sodium and potassium glasses, which exhibit the corresponding metallic electrode functions. However, this glass proved to be very refractory—the batch did not melt even at a temperature of 1500°. To lower the melting temperature and the viscosity of the glass, aluminum oxide and part of the silica were replaced by boric anhydride. To increase the chemical durability of the glass, a small amount (5%) of calcium oxide was added. Two rubidium glasses were melted, containing 20-30% B_2O_3 (glasses Nos. 5 and 6 in Table 1). But these glasses also proved still very viscous. To lower the viscosity, part of the calcium oxide was replaced by magnesium oxide. As a result, rubidium and cesium glasses of two compositions were synthesized: 60% SiO_2, 20% B_2O_3, 15% R_2O, 2% MgO, 3% CaO and 50% SiO_2, 30% B_2O_3, 15% R_2O, 2% MgO, 3% CaO, where R_2O = Rb_2O and Cs_2O (glasses Nos. 8, 9, 10, 11).

Table 1

Compositions of the synthesized glasses*

Glass No.	Mol. %, SiO_2	Mol. %, B_2O_3	Mol. %, Na_2O	Mol. %, K_2O	Mol. %, Rb_2O	Mol. %, Cs_2O	Mol. %, MgO	Mol. %, CaO	Wt. %, SiO_2	Wt. %, B_2O_3	Wt. %, Na_2O	Wt. %, K_2O	Wt. %, Rb_2O	Wt. %, Cs_2O	Wt. %, MgO	Wt. %, CaO
1	60	20	15				2	3	58,35	22,55	15,06				1,31	2,72
2	50	30	15				2	3	47,89	33,31	14,83				1,28	2,68
3	60	20		15			2	3	54,13	20,92		21,21			1,21	2,53
4	50	30		15			2	3	44,47	30,93		20,92			1,19	2,49
5	60	20			15			5	44,59	17,23			34,70			2,47
6	50	30			15			5	36,72	25,55			34,29			3,43
7	65	15			15		2	3	48,79	13,05			35,05		1,01	2,10
8	60	20			15		2	3	44,77	17,30			34,84		1,00	2,09
9	50	30			15		2	3	36,87	25,65			34,43		0,99	2,07
10	60	20				15	2	3	38,05	14,71				44,60	0,85	1,78
11	50	30				15	2	3	31,39	21,84				44,17	0,84	1,76
12	40	40				15	2	3	24,86	28,82				43,84	0,83	1,74

* The compositions are given according to synthesis data.

It should be noted that it is possible to obtain glasses of intermediate composition—for example, containing 25% B_2O_3. An attempt was also made to obtain a rubidium glass with a lower content of boric anhydride (No. 7) and a cesium glass with a higher content (No. 12). However, these glasses crystallized readily. For comparison, sodium and potassium glasses of the same composition were melted (Nos. 1, 2, 3, 4). Thus the synthesized glasses constitute two series, containing 20 (series I) and 30% (series II) boric anhydride.

---

* Here and below, the compositions of all glasses are given in mole percent.

For preparing the batch, metal carbonates, boric acid, and silicon dioxide were used. Sodium, potassium, and rubidium glasses were melted in small platinum crucibles in a silite furnace with four rods at a temperature of 1200-1450°; cesium glasses were melted in corundum crucibles in a kryptol furnace at a temperature of 1600°. The rubidium and cesium glasses obtained have strong light refraction (“crystalline luster”).

Glasses of both series were subjected to preliminary investigation. For a comparative characterization of the glasses obtained, tests of their chemical resistance to water were carried out by the method of Kohlrausch ([4]), which requires a small quantity of glass. This method is based on measuring the electrical conductivity of water after shaking glass powder in it. The glass was ground in an agate mortar. The fraction passing through a 200-mesh sieve was taken; the powder was then freed from dust by washing with ether. The results of the experiments are given in Table 2. For comparison, the chemical resistance of 3 electrode glasses, exhibiting a metallic-electrode function over a wide pH interval, was determined.

The values of specific electrical conductivity are given in the table with a correction for the initial electrical conductivity of the water, and the values of the quantity Δ, which characterizes the depth of destruction of the glass ([5],[6]):

$$\Delta = \frac{\delta F d}{v} = \frac{\chi - \chi_0}{\frac{p}{100A}\lambda^{18}_{\mathrm{ROH}}},$$

where δ is the thickness of the destroyed layer, F is the total surface area of the glass, d is the density of the glass, v is the volume of water, and $\chi - \chi_0$ is the specific electrical conductivity

alkali that has passed into solution, p is the percentage content of R_2O, A is the equivalent weight of R_2O, and $\lambda^{18}_{\mathrm{ROH}}$ is the equivalent electrical conductivity of the alkali at infinite dilution at 18°. If it is assumed that v, F, and d retain a constant value for all the glasses investigated, then the quantity Δ will be proportional to the thickness of the layer destroyed. For glasses available in large quantities, the chemical durability was determined by the accelerated method developed by the All-Union Scientific Research Institute of Glass (7). The results of these experiments, expressed in mg of R_2O, are also given in Table 2.

Table 2

Chemical durability of glasses at 18°

SovietRxiv

Glass composition, mol. %	Boiling time, h	$(x-x_0)\cdot10^{-6}$ (Na_2O)	$\Delta\cdot10^{-6}$ (Na_2O)	Na_2O, mg	$(x-x_0)\cdot10^{-6}$ (K_2O)	$\Delta\cdot10^{-6}$ (K_2O)	K_2O, mg	$(x-x_0)\cdot10^{-6}$ (Rb_2O)	$\Delta\cdot10^{-6}$ (Rb_2O)	$(x-x_0)\cdot10^{-6}$ (Cs_2O)	$\Delta\cdot10^{-6}$ (Cs_2O)
60% SiO_2; 20% B_2O_3; 15% R_2O; 2% MgO; 3% CaO	1	21.9	20.6		26.3	24.4	0.58	33.5	37.2	20.0	26.4
60% SiO_2; 20% B_2O_3; 15% R_2O; 2% MgO; 3% CaO	2	30.0	28.3		30.6	28.4	0.58	44.5	49.5	28.0	36.9
50% SiO_2; 30% B_2O_3; 15% R_2O; 2% MgO; 3% CaO	1	85.7	82.3		82.7	78.0		59.0	69.5	12.0	17.8

Glass composition, mol. %	Boiling time, h	$(x-x_0)\cdot 10^{-6}$ (Na_2O)	$\Delta\cdot 10^{-6}$ (Na_2O)	Na_2O, mg	$(x-x_0)\cdot 10^{-6}$ (K_2O)	$\Delta\cdot 10^{-6}$ (K_2O)	K_2O, mg	$(x-x_0)\cdot 10^{-6}$ (Rb_2O)	$\Delta\cdot 10^{-6}$ (Rb_2O)	$(x-x_0)\cdot 10^{-6}$ (Cs_2O)	$\Delta\cdot 10^{-6}$ (Cs_2O)
50% SiO_2; 30% B_2O_3; 15% R_2O; 2% MgO; 3% CaO	2	130.0	125.0		129.5	122.0		108.0	120.0	15.9	23.3
71% SiO_2; 11% B_2O_3; 3% Al_2O_3; 15% R_2O	1	16.8	16.2	0.22	17.1	16.2	0.19				
71% SiO_2; 11% B_2O_3; 3% Al_2O_3; 15% R_2O	2	18.3	17.6	0.22	20.4	19.2	0.19				
66% SiO_2; 9% B_2O_3; 5% Al_2O_3; 20% R_2O	1			0.36*	37.1	27.2	0.54				

SovietRxiv

Glass composition, mol. %	Boiling time, h	$(x - x_0) \cdot 10^{-6}$ (Na_2O)	$\Delta \cdot 10^{-6}$ (Na_2O)	Na_2O, mg	$(x - x_0) \cdot 10^{-6}$ (K_2O)	$\Delta \cdot 10^{-6}$ (K_2O)	K_2O, mg	$(x - x_0) \cdot 10^{-6}$ (Rb_2O)	$\Delta \cdot 10^{-6}$ (Rb_2O)	$(x - x_0) \cdot 10^{-6}$ (Cs_2O)	$\Delta \cdot 10^{-6}$ (Cs_2O)
66% SiO_2; 9% B_2O_3; 5% Al_2O_3; 20% R_2O	2			0.36*	40.7	30.0	0.54				
61% SiO_2; 9% B_2O_3; 5% Al_2O_3; 25% R_2O	1			1.55*	145.0	86.5	7.02				
61% SiO_2; 9% B_2O_3; 5% Al_2O_3; 25% R_2O	2			1.55*	167.0	100.0	7.02				

* Data taken from the work of M. M. Shults and L. G. Aio (8).

Comparing the quantities characterizing chemical durability, it may be noted that, in the case of glasses with a high content of boric anhydride, sodium and potassium glasses have approximately the same durability, whereas in electrode aluminoborosilicate glasses the durability of sodium glasses is higher than that of potassium glasses. Rubidium glass of series I is less durable, and that of series II more durable, than sodium and potassium glasses. Cesium glasses, especially in series II, are considerably more durable than glasses of analogous composition containing other alkali ions. It is possible that the increase in durability of the cesium glasses is connected with the transfer of a small amount of alumina into the glass from corundum crucibles. An aluminum impurity in these glasses was detected by spectral analysis.

Fig. 1. Sorption of rubidium ions on various glasses: 1 —sodium, 2 —potassium, 3 —rubidium, 4 —potassium electrode

Figure 1: Fig. 1. Sorption of rubidium ions on various glasses: 1 —sodium, 2 —potassium, 3 —rubidium, 4 —potassium electrode

To characterize the electrode properties of the glasses obtained, preliminary measurements of potentials were carried out in sodium chloride solutions with an electrode made of glass No. 1, and the resistance of electrodes made of potassium glass No. 3 was measured; it proved to be very high (10^5 MΩ). Measurements of the potential revealed its clear dependence on the concentration of sodium ions, but the sodium function was fulfilled only to 80-90% of the theoretical value.

To clarify the nature of the interaction of the glasses obtained with solutions, it is also of interest to investigate the absorption by these glasses cations. Such a study can provide some information on the nature of the bonding of alkali ions in glass. In connection with this, the sorption of rubidium ions on glasses of series II (Nos. 2, 4, and 9) in a 0.01 *n* solution of RbCl was studied by the tracer-atom method. The isotope Rb^{86} ($T = 19.5$ days) was used as the radioactive indicator. The results of the experiments, expressed as the number of rubidium atoms absorbed over a definite interval of time by a glass plate (the area of the working surface was approximately 1.5 cm^2), are given in Fig. 1. For comparison, the same graph shows the sorption of rubidium on potassium electrode glass (61% SiO_2, 9% B_2O_3, 5% Al_2O_3, 25% K_2O).

The results obtained are qualitative in character, since the relative measurement error with the chosen method of preparing the glass plates was approximately 25%. Therefore they make it possible to judge only the general character of the process.

Fig. 1. Sorption of rubidium ions on various glasses: 1 —sodium, 2 —potassium, 3 —rubidium, 4 —potassium electrode.

As can be seen from Fig. 1, the absorption of rubidium on sodium and potassium glasses is approximately the same and is somewhat greater than on rubidium glass, which, apparently, is a consequence of differences in the surface properties and internal structure of these glasses.

Thus, as a result of the work carried out, ratios of components have been found that ensure the production of glasses with a high content of rubidium and cesium oxides. This was achieved by introducing into the glass composition a large amount of boric anhydride in a mixture of magnesium and calcium oxides. On the basis of this first experiment, ways may be outlined for obtaining rubidium and cesium glasses possessing metallic electrode functions.

In conclusion, the authors express their deep gratitude to Prof. B. P. Nikol' skii for his constant attention and interest in the work, and also to Academician

SovietRxiv

of the Academy of Sciences of the BSSR M. A. Bezborodov and Prof. A. I. Avgustinik for valuable advice.

Leningrad State University
named after A. A. Zhdanov

Received
19 XI 1956

REFERENCES

1. S. Waterton, W. Turner, *J. Soc. Glass Techn.*, **18**, 268 (1934).
2. G. Perley, *Anal. Chem.*, **21**, 395 (1949).
3. F. Kracek, *J. Am. Chem. Soc.*, **52**, 1436 (1930).
4. F. Kohlrausch, *Wied. Ann.*, **44**, 577 (1891).
5. A. G. Samartsev, V. S. Molchanov, *Zhurn. opt.-mekh. prom.*, **9**, No. 8, 7 (1939).
6. V. S. Molchanov, *ZhFKh*, **13**, 934 (1940).
7. T. E. Gol' ba, *Glass Blowing*, 1938, p. 85.
8. M. M. Shul' ts, L. G. Aio, *Vest. LGU*, **10**, No. 8, 153 (1955).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.